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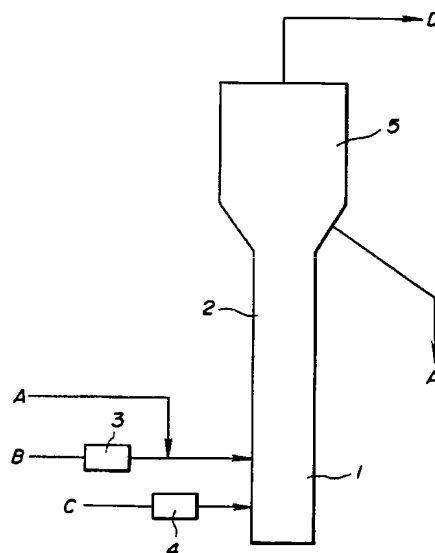
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(54) Method for purifying fine particulate silica

(57) Crude fumed silica resulting from pyrogenic hydrolysis is purified by continuously feeding particulate silica and steam or a mixture of steam and air in a steam/air volume ratio of at least 1/2 through an upright column from its bottom toward its top for forming a fluidized bed within the column at a gas linear velocity of 1 to 10 cm/sec. and a temperature of 250 to 600°C, whereby steam deprives the particulate silica of the halide borne thereon, and removing fine particulate silica from which the halide has been eliminated from the top of the column. Using a simple apparatus, pure fine particulate silica is collected at a low cost of energy consumption.

FIG.1



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## Description

This invention relates to a method for purifying fine particulate silica such as fumed silica by eliminating halide therefrom.

Fumed silica is widely used in the art as a filler for silicone elastomers and various other resins. In general, fumed silica is prepared by pyrogenic hydrolysis of silicon-containing halides. Since fumed silica has high surface activity and a large specific surface area, it has adsorbed thereon a substantial amount of hydrogen halide resulting from pyrogenic hydrolysis as a by-product. Fumed silica bears halogen in a chemically bonded state if the reaction is incomplete. It is undesirable to use fumed silica bearing a noticeable amount of halogen as a filler without treatment. Usually, such fumed silica is used after deacidifying treatment is carried out for eliminating the halide.

Conventionally, fumed silica is deacidified by using an endless steel belt or a rotary column with transfer means for bringing fumed silica in contact with wet air at 200 to 500°C as disclosed in Japanese Patent Publication (JP-B) No. 46274/1972. Although deacidification can be done at relatively low temperatures, the apparatus includes mechanical movable parts which tend to fail during use in a hot acidic corrosive atmosphere.

Another known deacidifying method is countercurrent contact between fumed silica and wet air as disclosed in JP-B 13832/1973. Although this method avoids to place mechanical movable parts in a hot acidic corrosive atmosphere and allows for use of a relatively simple apparatus, the method is less efficient in that separation of coarse particles cannot be accomplished concurrently with the deacidification. The treating temperature is relatively high. JP-B 13832/1973 describes a comparative example using a parallel flow fluidized layer. It is described that this parallel flow fluidized layer is at a temperature of 600 to 800°C. Use of such high temperature is impractical because the material of the apparatus and the heat source are limited.

The general aim herein is the provision of new and useful processes for purifying particulate silica.

A preferred aim in view of the prior art is to provide a method for purifying fine particulate silica which uses a relatively simple apparatus in the form of a fluidized bed, carries out deacidification in a forward flow fluidized bed at relatively low temperatures, and concurrently accomplishes separation of coarse particles.

We have found that deacidification of particulate silica can be carried out at relatively low temperatures by feeding particulate silica and a higher proportion of steam to form a forward flow fluidized bed. More particularly, when steam or a mixture of steam and air in a volume ratio of 0.5/1 or higher is fed along with particulate silica, preferably with gas linear velocity of 1 to 10 cm/sec., to form a forward flow fluidized bed with particulate silica, effective deacidification takes place even at a fluidized bed temperature of 250 to 600°C. The thus

established fluidized bed apparently reduces silica agglomeration therein, promotes diffusion of halide to the deacidifying gas or steam, and thus achieves efficient treatment.

According to one aspect herein there is provided a method for purifying fine particulate silica comprising the steps of continuously feeding halide-bearing fine particulate silica and steam or a mixture of steam and air in a volume ratio of 0.5/1 or higher through an upright column from its bottom toward its top for forming a fluidized bed within the column at a gas linear velocity of 1 to 10 cm/sec. and a temperature of 250 to 600°C, whereby steam causes the halide to be eliminated from the fine particulate silica, and removing the fine particulate silica from which the halide has been eliminated from the top of the column.

## BRIEF DESCRIPTION OF THE DRAWINGS

These and further features of the present invention will be apparent with reference to the following description and drawings, wherein:

the only figure, FIG. 1 schematically illustrates a system used in the practice of the method of the invention.

## DETAILED DESCRIPTION

Referring to FIG. 1, a method for purifying fine particulate silica uses a generally upright column 1 for forming a fluidized bed therein. To the bottom of the column 1 are connected a silica line A for providing crude fine particulate silica, an air line B for providing air, and a steam line C for providing steam or steam and air. To the top of the column 1 is formed a space 5 for preventing silica particles from scattering and stabilizing the surface of silica particles which is, in turn, connected to a silica removal line A' and a gas discharge line D. Crude fine particulate silica, typically fumed silica and steam or steam and air are fed through the lines A, B and C into the column 1 at the bottom so as to flow vertically upward from the bottom toward the top. A forward flow fluidized bed 2 is created in the column 1. The treated or deacidified fine particulate silica is removed from the column top to line A'. Preheaters 3 and 4 are disposed in the lines B and C. It is noted that the line C is described as a steam line although a mixture of steam and air may be passed through the line C.

The gas used to form the fluidized bed 2 is either steam alone or steam and air, the latter being typical.

Any of well-known methods such as pneumatic transportation may be employed for admitting crude fine particulate silica into the column 1 at its bottom. Typically silica is admitted into the column 1 by carrying it with air along line B as shown in FIG. 1. The amount of silica fed may be properly determined. Silica is preferably fed so as to provide 0.0002 to 0.02 g of silica, more preferably 0.001 to 0.01 g of silica per cubic centimeter of the

fluidized bed because effective treatment is expectable in this range.

As the gas for forming the fluidized bed 2 for treating crude fine particulate silica, steam, typically a mixture of steam and air is admitted into the column 1 at its bottom as shown in FIG. 1. According to the present invention, the proportion of steam is made high. Where air is used to carry silica to the column interior, the amount of entire steam is at least 0.5 volume, preferably 0.8 volume, more preferably at least 1 volume, most preferably more than 1 volume per volume of entire air. That is, a gas mixture of steam and air in a volume ratio of at least 0.5/1 is fed to form the fluidized bed 2. If the proportion of steam is below this limit, effective deacidifying treatment does not take place and the temperature of the fluidized bed must be increased.

The fluidized bed 2 is formed such that the fluidized bed-forming gas consisting of steam or steam and air has a linear velocity of 1 to 10 cm/sec., preferably 3 to 5 cm/sec. A linear velocity below this may fail to achieve full fluidization whereas above the range, silica particles are scattered away.

Also the fluidized bed 2 is maintained at a temperature of 250 to 600°C, preferably 250 to 500°C. Temperatures below 250°C lead to very slow deacidification, require a longer time to complete the treatment, and are thus impractical. Temperatures above 600°C can damage the material of the column 1, require a special heat source and are disadvantageous from the aspect of energy cost. More particularly, for a typical fluidized bed-forming column made of aluminum which has a melting point of 660°C, operation at 600°C or lower is required, and operation at 500°C or lower is required if local overheating is taken into account. If deacidification is possible at 350°C or lower, hydrocarbons can be used as thermal media. As compared with thermal media of inorganic salts, the use of hydrocarbon media eliminates operational trouble and reduces the system cost. Since the present invention enables operation at 350°C or lower, these advantages are available as well as a reduced cost of energy.

In order to maintain the fluidized bed at the selected temperature, the zone of the column 1 where the fluidized bed is formed is provided with heating means (not shown). It is also recommended to preheat steam and air prior to entry to the column 1. The preheaters 3 and 4 are located in the lines B and C to this end.

In the thus created fluidized bed 2, deacidification is carried out on the crude fine particulate silica. That is, steam traps or catches halides such as hydrogen halides which have been adsorbed to silica particles. The treating time is preferably 1/2 to 120 minutes, especially 1 to 20 minutes. Through such treatment, pure silica having a halogen content of 20 ppm or less is readily available.

The thus deacidified or purified silica is removed from the top of the column 1 and collected through the line A'. The gas consisting of steam or steam and air

from which silica has been separated is discharged from the column top to the line D. In order to prevent silica particles from scattering and stabilize the surface of powder, the space 5 of dilated diameter is disposed above the fluidized bed-forming zone of the column 1 as a precipitation/separation section.

As mentioned above, the present invention achieves the elimination of halide impurities from fine particulate silica at a reduced cost of energy using a simple apparatus. At the same time as deacidification takes place, fine particles which are lifted to the column top and collected through the outlet to the line A' are separated from large particles which do not reach the column top.

#### EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

#### Example 1

A column having an inner diameter of 8 cm was set upright as shown in FIG. 1. Its fluidized bed zone was heated and maintained at a temperature of 300°C. From the bottom of the column, 140 g/h of fumed silica resulting from pyrogenic hydrolysis (specific surface area 195 m<sup>2</sup>/g, chlorine content 1,162 ppm), 0.15 Nm<sup>3</sup>/h of air preheated to 300°C, and 0.15 Nm<sup>3</sup>/h of steam preheated to 300°C were continuously fed into the column to form a fluidized bed within the column at a linear velocity of 3.4 cm/sec. and a temperature of 300°C where the fumed silica was deacidified. Part of air was used to carry the fumed silica into the column. The thus purified fumed silica was separated from the used gas at the column top and taken out of the column. The time of deacidifying treatment was 7 minutes. By the treatment, the chlorine content of fumed silica was reduced to 14 ppm, indicating satisfactory deacidification.

#### Example 2

The procedure of Example 1 was repeated except that the fluidized bed was maintained at a temperature of 500°C, 280 g/h of fumed silica, 0.15 Nm<sup>3</sup>/h of air, and 0.15 Nm<sup>3</sup>/h of steam were fed, and the treating time was 3 minutes. By the treatment, the chlorine content of fumed silica was reduced to 6 ppm.

#### Comparative Example 1

The procedure of Example 1 was repeated except that the fluidized bed was maintained at a temperature of 300°C, 140 g/h of fumed silica, 0.25 Nm<sup>3</sup>/h of air, and 0.05 Nm<sup>3</sup>/h of steam were fed, and the treating time was 7 minutes. The thus purified fumed silica had a chlorine content of 68 ppm, indicating short deacidification.

Although some preferred embodiments have been

described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the teachings herein, the invention may be practiced otherwise than as specifically described.

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### Claims

1. A method for purifying fine particulate silica comprising the steps of: 10

continuously feeding halide-bearing fine particulate silica, air and steam through an upright column from its bottom toward its top for forming a fluidized bed within the column at a gas linear velocity of 1 to 10 cm/sec. and a temperature of 250 to 600°C, the volume ratio of steam to air being at least 0.5/1, whereby steam causes the halide to be eliminated from the fine particulate silica, and 15  
removing the fine particulate silica from which the halide has been eliminated from the top of said column. 20

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2. A method for purifying fine particulate silica comprising the steps of:

continuously feeding halide-bearing fine particulate silica and steam through an upright column from its bottom toward its top for forming a fluidized bed within said column at a gas linear velocity of 1 to 10 cm/sec. and a temperature of 250 to 600°C, whereby steam causes the halide to be eliminated from the fine particulate silica, and 30  
removing the fine particulate silica from which the halide has been eliminated from the top of said column. 35

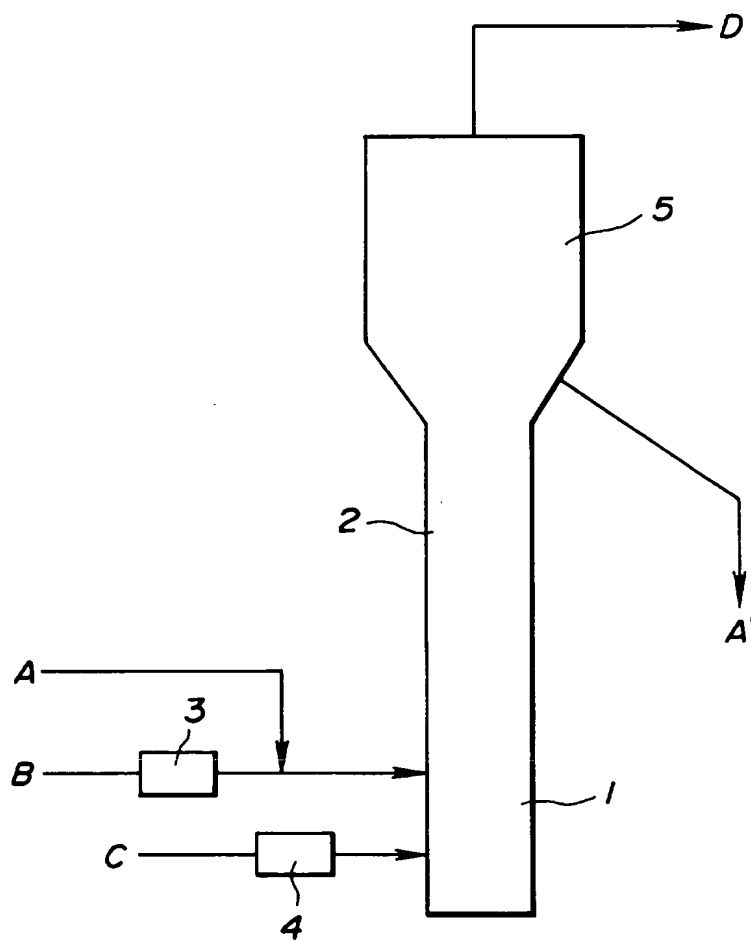
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FIG.1





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## EUROPEAN SEARCH REPORT

Application Number  
EP 95 30 7683

| DOCUMENTS CONSIDERED TO BE RELEVANT  |   |   |  |
|--|---|---|--|
| Category   | Citation of document with indication, where appropriate, of relevant passages             | Relevant to claim                                   | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| X  | DE-B-11 50 955 (DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER)<br>* claim 1 *  | 1,2   | C01B33/18                                    |
| A  | GB-A-1 197 271 (DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER)<br>* claim 1 * | 1   |  |
| D  | & JP-B-48 013 832   |   |  |
| A  | US-A-3 043 659 (W. HUGHES ET AL)<br>* claim 1 *   | 1,2   |  |
| A  | EP-A-0 044 903 (DEGUSSA AG)<br>* example 1 *  | 2   |  |
| The present search report has been drawn up for all claims   |   |   | TECHNICAL FIELDS SEARCHED (Int.Cl.6)         |
|  |   |   | C01B   |
| Place of search<br>BERLIN  |   | Date of completion of the search<br>8 February 1996 | Examiner<br>Clement, J-P                     |
| <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone<br/> Y : particularly relevant if combined with another document of the same category<br/> A : technological background<br/> O : non-written disclosure<br/> P : intermediate document</p> <p>T : theory or principle underlying the invention<br/> E : earlier patent document, but published on, or after the filing date<br/> D : document cited in the application<br/> L : document cited for other reasons<br/> &amp; : member of the same patent family, corresponding document</p> |   |   |  |

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